THE EFFECTS OF HYDROGEN ON OXYGEN SURFACE COMPLEXES DURING STEAM GASIFICATION

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Introduction

The effects of hydrogen on the population of oxygen surface complexes during steam gasification has been investigated for a phenol-formaldehyde resin char.

Experimental

Chars were prepared from synthesized resin at 1000°C for 2h in ultrapure flowing helium. A TGA system was adapted to perform the gasification experiments in 9 - 67% steam-helium mixtures. Post-gasification temperature programmed desorption (TPD) was performed in a different apparatus in flowing helium at 25 torr at a heating rate of 50K/min to 1100°C.

Results and Discussion

At lower temperatures from 400 to 600°C, only steam chemisorption occurred, rather than gasification, and the samples were quickly saturated in a matter of minutes, as determined from mass measurements. Figure 1 presents CO TPD spectra following steam chemisorption as a function of temperature in 50% steam-helium mixtures for 30 minutes. As shown, oxygen surface complexes are formed well below gasification temperatures.
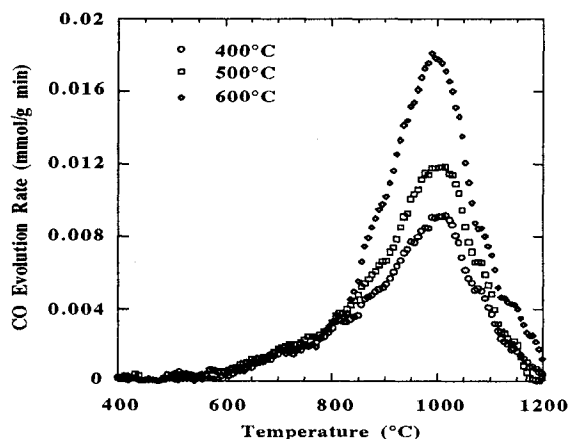
Figure 1. TPD spectra following steam chemisorption for 30 min. in 50% steam-helium mixtures.

Figure 2 presents CO TPD spectra following steam gasification in 50% steam-helium mixtures to 10% burn-off. In contrast to the preceding behavior, the amount of oxygen surface complexes decreases monotonically with increasing gasification temperature.
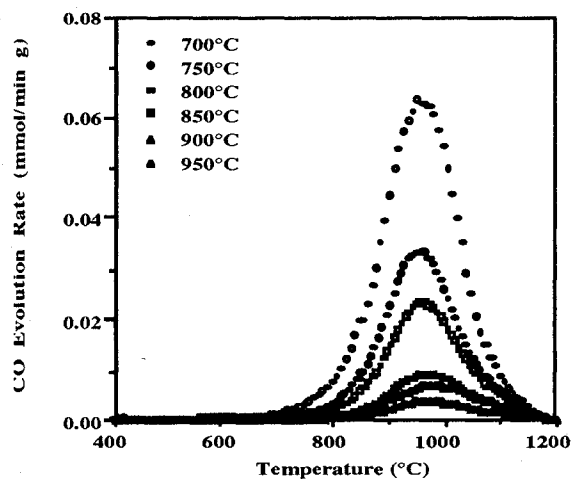
Figure 2. Post-gasification CO TPD spectra as a function of reaction temperature.

A comparison of the preceding two figures reveals some interesting behavior. The population of complexes desorbing up to about 800°C from the chemisorbed samples does not appear to change with increasing chemisorption temperature (cf. Figure 1). However, this low temperature CO evolution does not appear following steam gasification (cf. Figure 2). Therefore, either these surface sites become unsaturated at gasification temperatures, or the complexes are lost during the "quench process" [1]. From 800 to 1200°C, the shape of the CO evolution spectra in Figure 1 do not change very much with chemisorption temperature, although the population of oxygen surface complexes increases monotonically. These higher temperature surface complexes have the same desorption behavior as those formed during gasification (cf. Figure 2). Therefore, the same surface complexes formed at reaction temperatures can also be formed at lower chemisorption temperatures. In agreement with these general observations, Hermann and Hüttinger [2] reported that surface complexes can form at temperatures as low as 500°C; that they are extremely stable on PVC char; and that the population of surface complexes first increases with temperature up to 850°C, and decreases thereafter with increasing temperature.

Figure 3 presents hydrogen TPD spectra corresponding to the CO spectra in Figure 2. As shown, hydrogen evolution following steam gasification generally increases with gasification temperature from a total of about 6.4 mmol/g at 700°C to 9.4 mmol/g at 950°C. This increase in hydrogen evolution is accompanied by a decrease in oxygen evolution from 0.28 mmol/g at 700°C to 0.017 mmol/g at 950°C. The residual hydrogen content of the

resin char has been determined to be 0.8 wt %, or ~4.0 mmol/g [3]. Since all the chars in Figure 3 have this same bulk hydrogen content, and they were all exposed to the same partial pressure of steam, as well as (presumably) the same total amount of product hydrogen by 10% burn-off (i.e., ~50 mmol/g), this is interpreted to mean that hydrogen uptake increases with increasing gasification temperature. However, since the hydrogen evolution is large and of the same order of magnitude as the residual hydrogen content of the char, it is likely that a significant fraction of the hydrogen evolved upon TPD arises from residual bulk hydrogen in the char. In any case, it is apparent that a large amount of hydrogen also arises from hydrogen uptake during steam gasification; perhaps as much as 2.4 mmol/g at 700°C to 5.4 mmol/g at 950°C. These levels are well over an order of magnitude greater than oxygen evolution as CO, just as observed by Hüttinger and Merdes [4], Hermann and Hüttinger [2], and Lussier et al. [5].
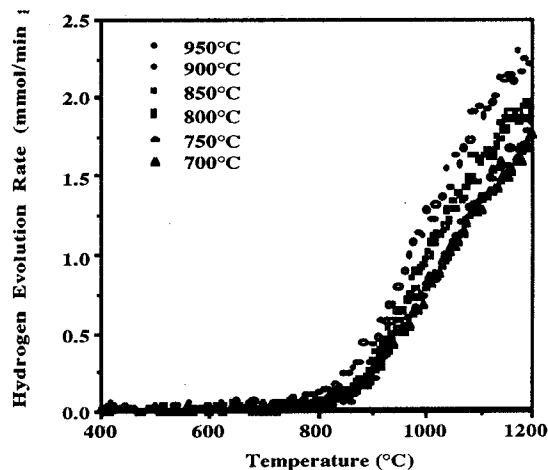

Figure 2. H_2 TPD spectra following gasification in 50% steam-helium mixtures as a function of temperature.

It has been demonstrated that hydrogen can directly reduce certain oxygen surface complexes and chemisorb on highly reactive "nascent" sites produced by the desorption of oxygen surface complexes [6]. Thus one possible explanation for the preceding behavior is that hydrogen competes favorably for the same "nascent" sites created by CO evolution. However, this cannot be true for all the active sites since this would imply that the steam gasification rate would decrease in time, as well as with temperature, such that steady-state would never be attained. In fact, of course, the steam gasification rate increases precipitously with temperature, and it always seems to attain a steady-state. Moreover, since the increase in hydrogen uptake is over an order of magnitude greater than the decrease in the oxygen surface complex population, hydrogen must also be taken up by sites where oxygen complexes do not form, and this process increases with temperature. The latter conclusion is along the lines suggested by Lussier et al. [5].

Yang and Yang [7] concluded that the reverse oxygen exchange reaction,

$$C(O) + H_2 \rightarrow H_2O + C_f, \qquad [R.1]$$
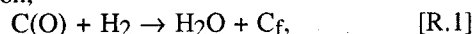
becomes the most important hydrogen inhibition mechanism at higher temperatures. Based on this, the following hypothesis is put forward to explain the current observations. The instantaneous selectivity between [R.1] and CO desorption, is

$$\gamma = \{k_{ex,o} [H_2]/k_{des,o}\}\exp(-[E_{ex}-E_{des}]/RT) \qquad [1]$$

where "ex" indicates the reverse oxygen exchange reaction, [R.1], and "des" indicates CO desorption. Thus, the sign of the difference of the activation energies controls the behavior of the selectivity with temperature. Assuming the desorption activation energies are distributed, then it stands to reason that the activation energies for reaction [R.1] will also be somewhat similarly distributed, since the distributions arise due to differences in the bond energies of the complexes on the char surface. Consequently, Eq.(1) indicates that for complexes with $E_{des} < E_{ex}$, reaction [R.1] will compete more favorably with surface complex desorption with increasing temperature, which will result in a decreasing population of oxygen surface complexes with temperature, which will be the most severe for the most stable, high temperature oxygen surface complexes. On the other hand, for $E_{des} > E_{ex}$, desorption will compete more favorably with reaction [R.1] with increasing temperature. It can be shown that if the distributions for the two activation energies overlap, with the mean and variance for reaction [R.1] being slightly greater than that for CO desorption, the net effect is that described above.

Conclusions

The preceding model of the effect of hydrogen on the oxygen surface complex population, plus the amplification of the reactivity of the surviving low temperature oxygen surface complexes due to the Arrhenius factor, can explain how the total amount of oxygen surface complexes can decrease due to competition with hydrogen chemisorption and reverse oxygen exchange, while the reactivity continues to increase.

Acknowledgments

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